Fabrication and characterization of $LiNi_xCo_{1-x}O_2$ thin-film for the cathode material of micro battery

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Introduction

Solid-state thin-film micro battery has been studied for various application fields. The most promising applications are the monolithic hybridization with CMOSRAM and combination with solar cells. Also, these micro batteries can be applied to microelectronics, sensor, and MEMS.

The research about thin film $LiNiO_2$ and $LiNi_{0.5}Co_{0.5}O_2$ was undergone in few numbers, and the most of thin film was not electrochemically active. The deposition of thin film was fabricated by the soft-solution method, which is similar to hydrothermal way, laser ablation, and sputtering. Via soft-solution method, the deposited film was electrochemically active but its surface morphology does not match the industrial needs.

In this study, $LiNi_xCo_{1-x}O_2$ thin films are deposited by the sputtering method using stoichiometric $LiNi_{0.5}Co_{0.5}O_2$ target with NiO. The effect of sputtering conditions, such as the partial pressure of plasma, flow rate of environment gases, time, power, and temperature, are reviewed on the basic film characteristics and their electrochemical properties. Also, the annealing conditions for the crystalline thin film are defined.

Experimental

To synthesize target material for sputtering, powder of $LiNi_{0.5}Co_{0.5}O_2$ was produced via solid-state reaction between $LiNO_3$ (Kanto, 99.95%, $NiCO_3$ (Cerac, 99.5%), $Co(NO_3)_2{\cdot}6H_2O$ (Strem, 99%) in the ratio of 1.05:0.5:0.5. Synthesized powder was pressed isostatically. Green body was sintered at 750ºC for 5 hours with uni-axially pressed at 25MPa in flowing O_2 atmosphere (150ml/min).

Thin-film deposition was undergone at room temperature and in the argon and oxygen atmosphere (4:1) with the different partial pressure, such as 1mTorr, 5mTorr, and 10mTorr, on the Pt (800Å) current collector / SiO_2 / Si (100) wafer by RF magnetron sputter at 100W power for 1 hour using sintered stoichiometric $LiNi_{0.5}Co_{0.5}O_2$ and NiO. As-deposited thin-film was an amorphous structure, and then annealed at 650, 750, 800ºC for 1 to 10 minutes in the oxygen environment.

For the electrochemical measurements, the $LiNi_xCo_{1-x}O_2$ thin film was placed in an open beaker cell containing 1M $LiClO_4$ in propylene carbonate (PC) solution, and lithium foil for counter and reference electrodes. This cell was placed in an Ar atmospheric glove box. Charge-discharge tests were controlled with an EGG electrochemical analysis system (Model 273A).

Results and discussion

Prepared powder from the solid-state reaction was good hexagonal structure (R3m), and showed no other impurity phases from the XRD analyses. The green density of sintering powder was over 75%, and the density of sintered body was over 99% of theoretical density.

As deposited thin-film was an amorphous structure, smooth surface and 20nm grain. The crystallinity of thin-film increased as the annealing temperature, but showed more coarse grain.

The electrochemical properties of film were characterized on its cyclic behavior and impedance spectra, and the composition of thin-film was measured by RBS and PIGE.

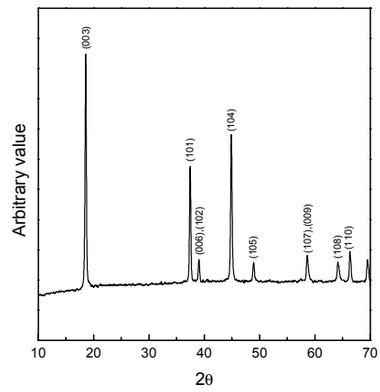

Fig. 1. XRD pattern of the sintering powder from solid-state reaction at 750°C for 5 hours with flowing of O_2 at 150ml/min.

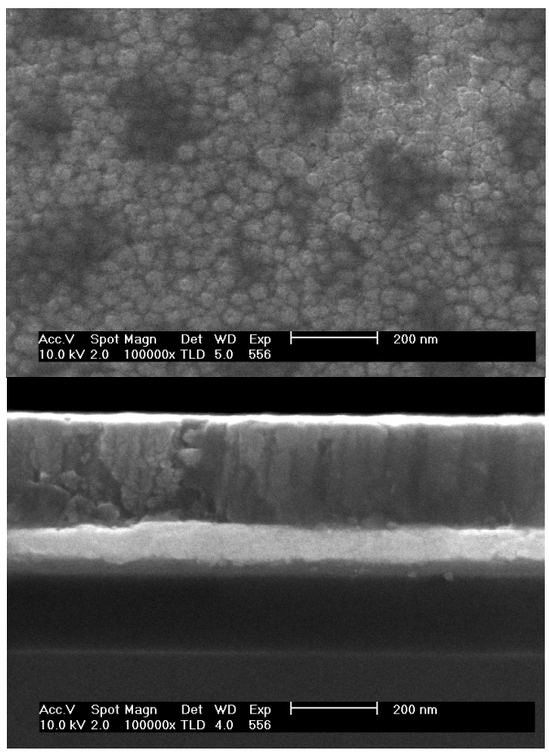

Fig. 2. Surface morphology and cross-sectional view of as deposited thin film with 5mTorr of Ar and O_2 (4:1) on Pt (500Å) / SiO_2 / Si (100) at 100W sputtering power for 1 hour.